

PATENT SPECIFICATION

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NO DRAWINGS

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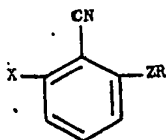
International Classification:—C 07 c (A 01 n)

COMPLETE SPECIFICATION

Substituted Benzonitriles, their preparation and Compositions containing them

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C3, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides a process for preparing a benzonitrile of the general formula



wherein X represents a chlorine or bromine atom, Z represents an oxygen or sulphur atom, or a sulphinyl SO or sulphonyl SO₂ group and R represents a hydrocarbon group which may be substituted by one or more of the following atoms or groups:— halogen, preferably chlorine, trifluoromethyl, nitro, amino, acylamino, hydroxy hydrocarbyloxy, the group OCH₂.CH₂.OR¹ (wherein R¹ represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms), carboxyl or hydrocarbyloxy carbonyl, which comprises treating a 2-chloro-6-nitrobenzonitrile or 2-bromo-6-nitrobenzonitrile with a compound of formula MZ¹R wherein M represents an alkali metal or ammonium, or with a mixture of a compound of formula HZ¹R and an alkali metal hydroxide, an alkali metal hydride, ammonia or ammonium hydroxide, Z¹ representing an oxygen or sulphur atom and R having the aforesaid meaning, and thereafter, if the corresponding sulphinyl derivative is required, oxidising the resulting thio derivative, or if the sulphonyl derivative is required, oxidising the corresponding thio or sulphinyl derivative.

The hydrocarbon group which R represents may be a saturated or unsaturated aliphatic hydrocarbon group, preferably of 1 to 4 carbon atoms, and preferably attached to Z by a primary or secondary carbon atom. R may also represent a cycloaliphatic hydrocarbon group, for example, a cyclohexyl group. R may also represent an araliphatic hydrocarbon group, the aliphatic portion preferably containing 1 to 4 carbon atoms and preferably being attached to Z by a primary or secondary carbon atom, for example, benzyl or phenylethyl. Preferably the hydrocarbon group represented by R is a mono- or poly-nuclear aromatic hydrocarbon group, for example, phenyl, naphthyl or diphenyl or an alkylated, preferably methylated derivative thereof, for example, tolyl or xylyl. These groups may be substituted as hereinbefore specified.

The hydrocarbyl radical of the hydrocarbyloxy or hydrocarbyloxy carbonyl substituent group may be a saturated or unsaturated aliphatic group, preferably of 1 to 4 carbon atoms, or it may be an aromatic radical for example, a phenyl radical.

Examples of groups represented by R are:— methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *isobutyl*, allyl, cyclohexyl, 2-hydroxyethylene, 2-methoxyethylene, ethoxycarbonylmethylene —CH₂.COOC₂H₅, phenyl, naphthyl, tolyl, xylyl. When R represents an aromatic nucleus attached directly to Z, it is preferable that in the reactant



- not more than one of the *ortho*-positions in the nucleus is substituted. The presence of two *ortho*-substituents, for example, chlorine or alkyl, appears to protect the group ZM or ZH and reduce its activity. Further examples of groups represented by R are *o*-, *m*-, or *p*-tolyl, 2,3-, 2,4-, 2,5- or 3,5-dimethylphenyl, 2-, 3- or 4-chlorophenyl, 2,4- or 3,5-dichlorophenyl, 2,4,5-trichlorophenyl, 2-, 3- or 4-nitrophenyl, 2-, 3- or 4-aminophenyl, 2-, 3- or 4-acetylaminophenyl, 2-, 3- or 4-methoxyphenyl and 2-, 3- or 4-ethoxyphenyl.
- The alkali metal compounds are preferably sodium or potassium compounds.
- The 2-halo-6-nitrobenzonitriles used as starting material may be obtained by the process claimed in Patent Specification No. 861,898. 2-Chloro-6-methoxybenzonitrile has previously been prepared from 2-chloro-6-methoxyaniline by a Sandmeyer reaction. The process of the present invention is an improvement on this previous method in that the starting material is readily available and, in general, yields are considerably higher.
- With the exception of 2-chloro-6-methoxybenzonitrile, the compounds obtainable by the process of the invention and covered by the above general formula are novel compounds.
- The process of the invention may be carried out by heating a mixture of the 2-halo-6-nitrobenzonitrile with the compound MZR or with a mixture of the compound HZR and an alkali metal hydroxide, M, Z and R having the aforesaid meanings, at a temperature in the range 120° to 250° C. and in the absence of a solvent.
- It is preferable, however, to carry out the process of the invention in a liquid reaction medium. When compounds of formula MZR or HZR, in which Z represents an oxygen atom, are used as reactants, it is convenient to use an excess of the hydroxy compound HOR as the reaction medium. Thus, 2-chloro-6-nitrobenzonitrile may be heated under reflux with potassium hydroxide in methanol or with sodium methoxide in methanol to give the corresponding 6-methoxy derivative. The homologues and analogues may be similarly prepared. Alternatively, the nitro compound may be heated with the alkali metal alkoxide in an inert liquid reaction medium, for example, diethyl diethylene glycol, dioxane or 1,2-dimethoxyethane, or a mixture of the hydroxy compound ROH and the inert liquid reaction medium may be used. The above mentioned inert liquid reaction media are also suitable for use when the nitro compound is reacted with a compound MZR or HZR where Z represents a sulphur atom. In some cases an alcohol, for example, methanol, may be used.
- The 2-halo-6-nitrobenzonitrile and the compound MZR or HZR are preferably employed in approximately equimolecular proportions. Since however ammonia is readily lost from the hot reaction mixtures in which ammonia or ammonium hydroxide is used, unless these are in a closed vessel, it is convenient to pass ammonia gas through the reaction mixture during the course of the reaction.
- The alkali metal compound MZR may be prepared in any way known in the art for preparing such compounds. A convenient method is to react the compound HZR with a stoichiometric amount of an alkali metal hydroxide, for example, sodium methoxide, in excess of the alcohol used to prepare the alkoxide, and then, if necessary, evaporate to dryness. The residual alkali metal compound may then be taken up in the liquid reaction medium. Where the compound HZR contains substituents which are hydrolysed by alkali metal alkoxides, the compound MZR can be prepared by reacting the compound HZR with an alkali metal hydride.
- In general, the reactants are heated together for several hours at atmospheric pressure, but the reaction time can be shortened when a liquid reaction medium is used by heating the mixture at a higher temperature in an autoclave, or by using a high boiling liquid reaction medium, for example, diethyl diethylene glycol.
- When reaction is complete, the liquid reaction medium is removed by distillation, preferably under reduced pressure. The residue is then washed with water to remove water soluble impurities and the residue may then be crystallised from a solvent, for example, methanol, ethanol, light petroleum or benzene. In some cases, it may be desirable to extract the above residue with a solvent, for example, benzene, light petroleum or alcohol. If necessary, the extract is then concentrated and on cooling the desired benzonitrile derivative separates in crystalline form.
- Compounds of the invention in which R contains a carboxyl group are preferably prepared by hydrolysing the corresponding carboxylic ester.
- Compounds containing acylamino substituents in the group R may be prepared directly from the reactant MZR or HZR in which R contains such an acylamino substituent or indirectly by first preparing a compound according to the invention in which R contains an amino group and subsequently acetylating it.
- Compounds of the above general formula in which Z represents a sulphinyl SO or sulphonyl SO₂ group are prepared by oxidising the corresponding compounds in which Z represents a sulphur atom with a substance known to bring about oxidation of a sulphide to a sulphoxide or sulphone. Such substances include hydrogen peroxide, peroxides, persalts (for example alkali metal permanganates), peracids, particularly percarboxylic acids such

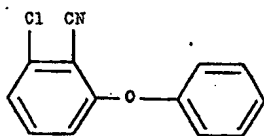
as peracetic acid or mixtures of hydrogen peroxide and a carboxylic acid such as acetic acid.

The reaction is preferably carried out in an organic solvent medium, for example, in acetic acid or in acetone. When it is desired to obtain the sulphonyl derivative, the theoretical quantity or a slight excess of the oxidising agent is employed, preferably at room temperature, for example, at a temperature in the range 15° to 25° C. In general, a reaction time of some days, for example, 2 to 4 days, is required. When the corresponding sulphonyl derivative is to be prepared, the theoretical quantity of oxidising agent may be used but it is advantageous to employ an excess, for example up to 100% excess. The reaction may be carried out at room temperature for some days, for example, 2 to 4 days, or a temperature up to about 60° C may be employed when the reaction is more complete and more rapid. The sulphonyl derivatives may also be prepared by oxidising the corresponding sulphonyl compounds under conditions similar to those employed in oxidising the thio derivative.

The following examples illustrate the novel compounds of the invention and their preparation, parts by weight (w) and parts by volume (v) bearing the same relation as the kilogram and the litre.

EXAMPLE 1.

Preparation of 2-chloro-6-phenoxybenzonitrile.



A mixture of sodium methoxide (54 w) and phenol (94w; 1 mol.) in methanol (500v) was evaporated to dryness and the sodium phenoxide taken up in a 1:2-dimethoxyethane (500v). A solution of 2-chloro-6-nitrobenzonitrile (183w; 1 mol.) in 1:2-dimethoxyethane (2,000v) was added and the mixture heated at 95° C under reflux overnight (about 16 hours). The precipitate was filtered off and the filtrate evaporated under reduced pressure to dryness. The residue was shaken with water (5,000v) and the resulting solid was collected, dried and crystallised from light petroleum (40°/60°) to give colourless prisms (108w), m.p. 59° to 60° C.

Analysis

Found N 10.4, Cl 12.8%
C₁₃H₉O₂N₂Cl requires N 10.2, Cl 12.9%.

Analysis Found C 67.7, H 3.5%
C₁₃H₈ONCl requires C 68.0, H 3.5%.

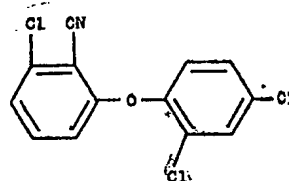
EXAMPLE 2.

Preparation of 2-chloro-6-phenoxybenzonitrile.

The preparation described in Example 1 was repeated using diethyl diethylene glycol as the reaction medium, and heating to reflux temperature (about 187° C) for 5 hours. After recrystallisation, 160w of colourless prisms, m.p. 59° to 60° C. was obtained.

EXAMPLE 3.

Preparation of 2-chloro-6(2,4-dichlorophenoxy)benzonitrile.



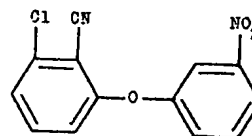
2-Chloro-6-nitrobenzonitrile (183w; 1 mol.) and sodium 2:4-dichlorophenoxide (185w; 1 mol) were heated together in 1:2-dimethoxyethane (3,000v) at refluxing temperature for 16 hours. The mixture was cooled and filtered and the filtrate distilled to dryness under reduced pressure. The residue was recrystallised twice from methanol to give colourless needles, m.p. 92° to 93° C. (Yield 112w; 37.5%).

Analysis

Found Cl 35.2%
C₁₃H₆ONCl₂ requires Cl 35.7%.

EXAMPLE 4.

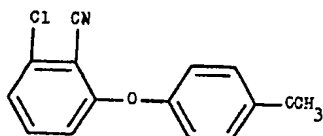
Preparation of 2-chloro-6-(3-nitrophenoxy)benzonitrile.



This compound was prepared by reacting 2-chloro-6-nitrobenzonitrile and sodium 3-nitrophenoxide in a manner similar to that described in Example 3. The crude product crystallised from methanol as colourless platelets, m.p. 132° to 133° C. Yield 38%.

EXAMPLE 5.

Preparation of 2-chloro-6-(4-methoxyphenoxy)benzonitrile.



To a solution of 2-chloro-6-nitrobenzonitrile (36.5w) in 1,2-dimethoxyethane (300v) was

Analysis Found C 64.6, H 3.9, Cl 13.9%
 $C_{11}H_{10}O_2NCl$ requires C 64.7, H 3.9, Cl 13.7%.

In an analogous manner were prepared:—

2 - Chloro - 6 - (2 - methoxyphenoxy)benzonitrile m.p. 92° to 93° C.

Analysis Found C 64.9, H 3.9, Cl 13.5%.

2 - Chloro - 6 - (3 - methoxyphenoxy)benzonitrile m.p. 82° to 83° C. Yield 64% theory.

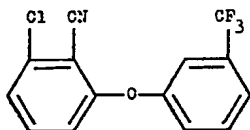
Analysis Found C 65.2, H 3.9, Cl 13.5%.

and 2 - Chloro - 6 - (3 - ethoxyphenoxy)benzonitrile m.p. 62° to 63° C. Yield 58% theory.

Analysis Found C 65.6, H 4.4, Cl 12.9%
 $C_{12}H_{12}O_2NCl$ requires C 65.8, H 4.4, Cl 13.0%.

EXAMPLE 6.

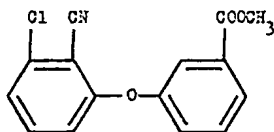
2-Chloro-6-(3-trifluoromethylphenoxy)benzonitrile.



Analysis Found N 4.6, Cl 11.4%
 $C_{14}H_7ONClF_3$ requires N 4.7, Cl 11.9%.

EXAMPLE 7.

2-Chloro-6-(3-methoxycarbonylphenoxy)benzonitrile.



Analysis Found C 62.5, H 3.3, Cl 12.0%
 $C_{15}H_{10}O_3NCl$ requires C 62.6, H 3.4, Cl 12.4%.

2-Chloro - 6 - (3 - carboxyphenoxy)benzonitrile was prepared by hydrolysing the ester produced according to Example 7 by warming with 5% aqueous sodium hydroxide solution until solution was complete. The solution was acidified with 3-N hydrochloric acid to give

Analysis Found C 61.6, H 2.9, Cl 13.0%
 $C_{14}H_8O_3NCl$ requires C 61.5, H 2.9 Cl 13.0%.

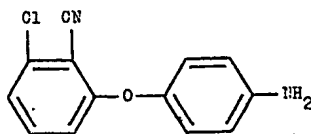
added a mixture of p-methoxyphenol (28.4w), sodium hydride (5w) and 1,2-dimethoxyethane (300v). A dark brown solution resulted. It was refluxed for 16 hours and then filtered free of precipitated sodium nitrite. The solvent was then removed by distillation and a large excess of water added to the residual orange-brown oil which solidified to a yellow solid, m.p. 45° to 48° C. This was recrystallised from light petroleum (40°/60° C) yielding colourless needles m.p. 51° to 52° C. Yield 27 w (51% theory).

was prepared by reacting 2-chloro-6-nitrobenzonitrile and sodium 3-trifluoromethylphenoxide in a manner similar to that described in Example 5. The crude reaction product was recrystallised from light petroleum (40°/60° C.) to yield yellow prisms m.p. 87° to 88° C. Yield 78% theory.

was prepared by reacting 2-chloro-6-nitrobenzonitrile and sodium 3-methoxycarbonylphenoxide in a manner similar to that described in Example 5. After recrystallisation from light petroleum (60°/80° C), the product had m.p. 101° to 102° C. Yield 41w (71% theory).

a white precipitate which was collected, washed with water and dried. After recrystallisation from industrial methylated spirit, the product had m.p. 240° to 241° C. Yield quantitative.

EXAMPLE 9.
2-Chloro-6-(4-aminophenoxy)benzonitrile.



Analysis Found C 64.0, H 4.0, Cl 14.6%
C₁₃H₉ON₂Cl requires C 63.8, H 3.7, Cl 14.5%.

- 15 Acetylation of the above amino compound by heating with a mixture of glacial acetic acid and acetic anhydride and recrystallisation of the product from benzene gave 2-chloro-6-(4-acetylamino phenoxy)benzonitrile as
20 yellow prisms, m.p. 158° to 159° C. Yield 88% theory.

Analysis Found C 63.5, H 3.8%
C₁₅H₁₁O₂N₂Cl requires C 62.9, H 3.8%.

- 35 Analysis Found C 59.0, H 2.6, Cl 27.0%
C₁₃H₇ONCl₂ requires C 59.2, H 2.6, Cl 26.9%.

- The compound was also obtained by passing dry chlorine into a solution of 2-chloro-6-phenoxybenzonitrile in boiling carbon tetra-
40 chloride for 8 hours. Yield 84% theory.

EXAMPLE 11.
2-Chloro-6-(2-chlorophenoxy)benzonitrile was prepared by reacting 2-chloro-6-

Analysis Found C 59.9, H 2.6, Cl 26.7%
C₁₃H₇ONCl₂ requires C 59.2, H 2.6, Cl 26.9%.

- 55 EXAMPLE 12.
2-Chloro-6-(4-tolyloxy)benzonitrile was prepared by reacting 2-chloro-6-nitrobenzonitrile and sodium 4-cresylate in a manner similar to that described in Example 5. The crude

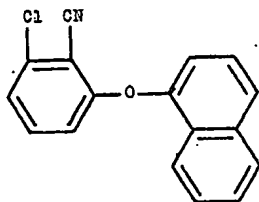
Analysis Found C 69.7, H 4.2, Cl 14.1%
C₁₄H₁₀ONCl requires C 69.0, H 4.1, Cl 14.6%.

- 65 In a similar manner was prepared 2-chloro-6-(3-tolyloxy)benzonitrile m.p. 59°—60° C. Yield 70% theory.

Analysis Found C 69.0, H 4.3, Cl 14.5%
C₁₄H₁₀ONCl requires C 68.9, H 4.1, Cl 14.6%.

70

EXAMPLE 13.
Preparation of 2-chloro-6-(1-naphthoxy)benzonitrile.



was prepared by reacting 2-chloro-6-nitrobenzonitrile and sodium 4-aminophenoxide in a manner similar to that described in Example 5. The crude product was extracted with light petroleum (60°/80° C) the solvent removed from the extract and the residue recrystallised from ethanol to yield yellow
10 shining plates, m.p. 116° to 117° C. Yield 76%.

EXAMPLE 10.

2-Chloro-6-(4-chlorophenoxy)benzonitrile was prepared by reacting 2-chloro-6-nitrobenzonitrile and sodium *p*-chlorophenoxide in a manner similar to that described in Example 5. The crude reaction product was extracted with light petroleum (40°/60° C), the solvent removed from the extract and the residue recrystallised from ethanol. The purified product had m.p. 111° to 112° C. Yield 78% theory.

nitrobenzonitrile and sodium 2-chlorophenoxide in a manner similar to that described in Example 5. The crude reaction product was extracted with light petroleum (40°/60° C), the solvent removed from the extract and the residue recrystallised from ethanol to give pale yellow needles m.p. 77° to 78° C. Yield 60% theory.

reaction product was extracted with light petroleum (60°/80° C), the solvent removed from the extract and the residue recrystallised from ethanol to give pale yellow needles m.p. 81° to 82° C. Yield 72% theory.

75 To a solution of 2-chloro-6-nitrobenzonitrile (36.5w) in 1,2-dimethoxyethane (250v) was added a mixture of 1-naphthol (28.8w), sodium hydride (5w) and 1,2-dimethoxyethane (250v). The mixture was refluxed for 8 hours, then filtered while hot to remove precipitated sodium nitrite. The solvent was then removed by distillation and water added to the residual oil. The resulting black precipitate (43w) was extracted in a Soxhlet
80

apparatus with cyclohexane, a pale yellow solid (11w; m.p. 84° to 86° C) being recovered from the extract. This solid was

recrystallised from ethanol to give 6.5w of product with m.p. 94° to 95° C. Yield 12% theory.

Analysis

Found C 72.6, H 4.0, Cl 12.5%
 $C_{17}H_{10}ONCl$ requires C 73.0, H 3.6, Cl 12.7%.

EXAMPLE 14.

10 2 - Chloro - 6 - (2 - naphthylloxy) benzonitrile was prepared in a manner analogous to that described in Example 13, except that the crude reaction product was extracted with

hexane. The off-white solid obtained from the extract (21 w, m.p. 121° to 123° C) was recrystallised from aqueous dioxane to give a product (16.2w) with m.p. 128° to 129° C. Yield 29% theory.

Analysis

20 Found C 72.9, H 3.3, Cl 12.9%
 $C_{17}H_{10}ONCl$ requires C 73.0, H 3.6, Cl 12.7%.

EXAMPLE 15.

Preparation of 2-chloro-6-methoxybenzonitrile.

25 A mixture of 2-chloro-6-nitrobenzonitrile (183w), potassium hydroxide (56) and methanol (1,500v) was refluxed for 5 hours and evaporated to dryness under reduced pressure. The residue was washed with water and extracted several times with hexane. The combined hexane extracts were evaporated to

small bulk and cooled when colourless plates (140w) were obtained, m.p. 114° C.

EXAMPLE 16.

Preparation of 2-chloro-6-allyloxybenzonitrile.

35 The process of Example 15 was repeated using allyl alcohol (1,500v) in place of methanol. The product crystallised from hexane as white plates (75w), m.p. 43° to 44° C.

Analysis

40 Found C 61.2, H 4.4, Cl 18.0%
 $C_{10}H_7ONCl$ requires C 62.1, H 4.1, Cl 18.4%.

EXAMPLE 17.

Preparation of 2-chloro-6-isopropoxybenzonitrile.

45 The process of Example 15 was repeated using isopropanol (1,500v) instead of methanol. The isopropyl ether (135w) was obtained as colourless platelets m.p. 51° to 52° C.

Analysis

50 Found C 61.1, H 5.2, N 7.3, Cl 18.2%
 $C_{10}H_{10}ONCl$ requires C 61.4, H 5.1, N 7.2, Cl 18.2%.

EXAMPLE 18.

Preparation of 2-chloro-6-isobutoxybenzonitrile.

Using isobutanol (1,500v) in place of methanol in Example 15 gave the isobutoxy derivative as pale yellow plates (210w), m.p. 62° to 63° C from hexane.

Analysis

Found C 62.8, H 5.6, N 7.2, Cl 17.4%
 $C_{11}H_{12}ONCl$ requires C 63.0, H 5.7, N 6.7, Cl 16.9%.

EXAMPLE 19.

Preparation of 2-chloro-6-(2-methoxyethoxy)benzonitrile.

60 When 2-methoxyethanol (1,500v) was used instead of methanol in Example 15, the product was obtained as white prisms from hexane or water, (145w) m.p. 60° C.

Analysis

65 Found C 56.9, H 5.1, Cl 16.7%
 $C_{10}H_{10}O_2NCl$ requires C 56.8, H 4.7, Cl 16.8%.

EXAMPLE 20.

Preparation of 2-chloro-6-(2-hydroxyethoxy)benzonitrile.

70 A solution of 2-chloro-6-nitrobenzonitrile (366w) in ethylene glycol (2,500v) was heated under reflux for 24 hours while dry ammonia was bubbled through the solution. Most of

the solvent was then distilled off under pressure and the residue was poured into water. On acidification with hydrochloric acid, a black tar precipitated. This was crystallised from benzene and yielded the desired product in the form of pale yellow prisms (100w), m.p. 110° to 111° C.

Analysis

Found C 54.5, H 4.1, N 7.1, Cl 17.6%
 $C_9H_8O_2NCl$ requires C 54.6, H 4.1, N 7.6, Cl 18.0%.

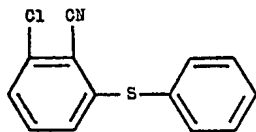
EXAMPLE 21.

Preparation of 2-chloro-6-benzoyloxybenzonitrile.

85 Using distilled benzyl alcohol (1,500v) in place of methanol in Example 15, the benzyl ether was obtained (44w), m.p. 97° to 98° C.

Analysis Found C 69.5, H 4.7%
 $C_{14}H_{10}ONCl$ requires C 69.1, H 4.2%.

EXAMPLE 22.
Preparation of 2-chloro-6-phenylthio-
benzonitrile.



5 Thiophenol (11.0w) was added to a mixture of sodium hydride (2.6w) and 1,2-

Analysis

$C_{13}H_8NSCl$ requires

Found C 63.5, H 3.4, S 13.2%

C 63.5, H 3.3, S 13.0%.

20

EXAMPLE 23.

2 - Chloro - 6 - (4 - tolylthio)benzonitrile was prepared by the method of Example 22 using 4-thiocresol instead of thiophenol. The

Analysis

$C_{14}H_{10}NSCl$ requires

Found C 65.1, H 4.0, S 12.7%

C 64.6, H 3.9, S 12.4%.

30

EXAMPLE 24.

2 - Chloro - 6 - (4 - chlorophenylthio)benzonitrile, was prepared by the method of Example 22 using 4-chlorothiophenol instead of thiophenol. The crude reaction product was recrystallised from light petroleum (60°/80° C) to give yellow prisms of m.p. 100° to 101° C. Yield 72% theory.

Analysis

$C_{13}H_7NSCl_2$ requires

Found S 11.7%

S 11.5%.

35

Analysis

$C_{10}H_8NSCl$ requires

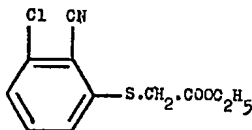
Found

C 57.5, H 4.1, Cl 17.7%

C 57.3, H 3.9, Cl 17.1%.

50

EXAMPLE 26.
Preparation of 2-chloro-6-(ethoxycarbonylmethylthio)benzonitrile.



55 2-Chloro-6-nitrobenzonitrile (91.2w) in dimethoxyethane (500v) was added gradually

Analysis

$C_{11}H_{10}O_2NSCl$ requires

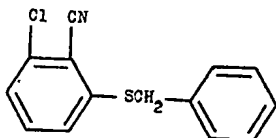
Found Cl 13.9, S 12.8%

Cl 13.9, S 12.6%.

70

EXAMPLE 27.

2-Chloro-6-(benzylthio)benzonitrile.



Analysis

$C_{14}H_{10}NSCl$ requires

Found C 65.8, H 4.0, Cl 13.8, S 11.8%

C 65.1, H 3.9, Cl 13.7, S 12.3%.

dimethoxyethane (300v) and the resulting mixture was added to 2-chloro-6-nitrobenzonitrile (18.5w) in 1,2-dimethoxyethane (250v). The mixture was refluxed for 8 hours. A solid separated which was filtered off. The solvent was distilled from the brown filtrate leaving a waxy residue which was extracted in a Soxhlet apparatus with light petroleum (40°/60° C.) Yellow crystals of m.p. 66° to 67° C were obtained from the extract. Yield 16w (70% theory).

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crude reaction product was recrystallised from light petroleum (60°/80° C), the product then having m.p. 114° to 115° C. Yield 46% theory.

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EXAMPLE 25.

2 - Chloro - (6 - allylthio)benzonitrile was prepared by the method of Example 22 using allyl thiol instead of thiophenol. The crude product was an oil which on solution in light petroleum (40°/60° C) and cooling gave a crystalline product m.p. 40° to 41° C. Yield 95% theory.

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to the sodium salt prepared from ethyl thioglycollate (60w) and sodium hydride (24w of 50% w/w) in dimethoxyethane (500v), cooling the mixture in ice-water when necessary. The mixture was refluxed for 24 hours (some nitrous fumes were evolved), filtered hot and the filtrate evaporated to small bulk. Water (1000v) was added to the residue and the resulting solid was collected and crystallised from aqueous methanol, clusters of fine needles, m.p. 84° C being obtained. Yield 30w.

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EXAMPLE 28.

Preparation of 2-chloro-6-(4-chlorobenzylthio)-benzonitrile.

5 A mixture of 4-chlorobenzyl mercaptan (26.3w), sodium hydride (3.9w) and 1,2-dimethoxyethane (200v) was added to 2-chloro-6-nitrobenzonitrile (29.5w) in 1,2-dimethoxyethane (200v). The mixture was refluxed for 12 hours, filtered while hot and

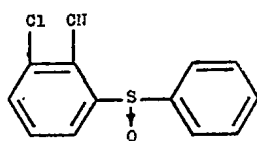
the solvent distilled off from the filtrate. The residual brown oil solidified when mixed with excess water. The solid was extracted with light petroleum (40°/60° C) and after evaporation of the solvent, the residue was recrystallised from light petroleum (60°/80° C). The product obtained had m.p. 130° to 131° C. Yield 31.4w (66% theory).

Analysis

Found C 57.4, H 3.1, S 11.4%
C₁₁H₉NSCl₂ requires C 57.2, H 3.1, S 11.0%.

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EXAMPLE 29.

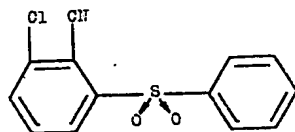
Preparation of 2-chloro-6-(phenylsulphonyl)-benzonitrile.

Analysis

Found C 59.7, H 3.3, Cl 13.7%
C₁₃H₉ONSCl requires C 59.6, H 3.1, Cl 13.6%.

Aqueous hydrogen peroxide (28% w/v, 9.5v) was added to 2-chloro-5-phenylthiobenzonitrile (19w; prepared according to Example 22) dissolved in glacial acetic acid (500v) and the mixture left at room temperature for 4 days. It was then evaporated to small bulk under reduced pressure and the residue added to water (500v). The resulting solid was collected and crystallised from a mixture of light petroleum (60°/80° C) and benzene. The product had m.p. 142° to 143° C. Yield 12.5w.

EXAMPLE 30.

2-Chloro-6-phenylsulphonylbenzonitrile.

Analysis

Found C 56.9, H 3.3, Cl 13.3%
C₁₃H₉O₂NSCl requires C 56.2, H 2.9, Cl 12.8%.

was prepared according to the process of Example 29 but using 23v of the aqueous hydrogen peroxide. Crystallisation of the reaction product from ethanol gave colourless prisms of m.p. 161° to 162° C. Yield 13.5w.

EXAMPLE 31.

Preparation of 2-chloro-6-ethylsulphonylbenzonitrile.

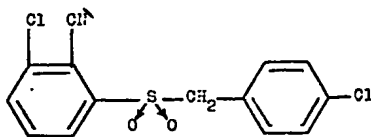
50 2-Chloro-6-ethylthiobenzonitrile (7w) was dissolved in glacial acetic acid (200 v) and 3 equivalents of aqueous hydrogen peroxide

(28% w/v) were added. The mixture was left for 4 days at room temperature and was then poured into excess of water. The resulting precipitate was dried and crystallised from light petroleum (60°/80° C) and then had m.p. 114° to 115° C. Yield 2.5w.

Analysis

Found C 47.7, H 3.7, N 14.1%
C₉H₉O₂NSCl requires C 47.1, H 3.5, N 13.9%.

EXAMPLE 32.

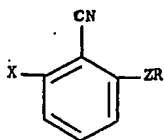
Preparation of 2-chloro-6-(4-chlorobenzylsulphonyl)benzonitrile.

Analysis

Found C 51.6, H 2.8, S 9.9%
C₁₄H₉O₂NSCl₂ requires C 51.5, H 2.6, S 9.8%.

Aqueous hydrogen peroxide (28% w/v; 15v) was added to a solution of 2-chloro-6-(4-chlorobenzylthio)benzonitrile (10w) in glacial acetic acid (300v) and the mixture left for 4 days at room temperature. The yellow solution was then distilled under reduced pressure to a final bulk of 150v. Water was added to the residue and the pale yellow precipitate was collected and dried. It was recrystallised from ethanol to give colourless needles, m.p. 178° to 179° C. Yield 10.5w (95% theory).

The present invention also relates to novel compounds of the general formula:



wherein X, Z and R have the meanings hereinbefore specified, but excluding 2-chloro-6-methoxybenzonitrile.

Specific examples of novel compounds of the above general formula are:—

- 2-chloro-6-allyloxybenzonitrile.
- 10 2-chloro-6-isopropoxybenzonitrile.
- 2-chloro-6-isobutoxybenzonitrile.
- 2-chloro-6-benzyloxybenzonitrile.
- 2-chloro-6-(2-methoxyethoxy)benzonitrile.
- 2-chloro-6-(2-hydroxyethoxy)benzonitrile.
- 15 2-chloro-6-phenoxybenzonitrile.
- 2-chloro-6-(2,4-dichlorophenoxy)benzonitrile.
- 2-chloro-6-(3-nitrophenoxy)benzonitrile.
- 2-chloro-6-(4-methoxyphenoxy)benzonitrile.
- 20 2-chloro-6-(3-methoxyphenoxy)benzonitrile.
- 2-chloro-6-(2-methoxyphenoxy)benzonitrile.
- 25 2-chloro-6-(3-ethoxyphenoxy)benzonitrile.
- 2-chloro-6-(3-trifluoromethylphenoxy)benzonitrile.
- 2-chloro-6-(3-methoxycarbonylphenoxy)benzonitrile.
- 30 2-chloro-6-(3-carboxyphenoxy)benzonitrile.
- 2-chloro-6-(4-aminophenoxy)benzonitrile.
- 2-chloro-6-(4-acetylaminophenoxy)benzonitrile.
- 35 2-chloro-6-(4-chlorophenoxy)benzonitrile.
- 2-chloro-6-(2-chlorophenoxy)benzonitrile.
- 2-chloro-6-(4-tolyloxy)benzonitrile.
- 2-chloro-6-(3-tolyloxy)benzonitrile.
- 2-chloro-6-(1-naphthylloxy)benzonitrile.
- 40 2-chloro-6-(2-naphthylloxy)benzonitrile.
- 2-chloro-6-(phenylthio)benzonitrile.
- 2-chloro-6-(4-chlorophenylthio)benzonitrile.
- 2-chloro-6-(4-tolylthio)benzonitrile.
- 45 2-chloro-6-benzylthiobenzenitrile.
- 2-chloro-6-allylthiobenzenitrile.
- 2-chloro-6-(ethoxycarbonylmethylthio)benzonitrile.
- 2-chloro-6-(4-chlorobenzylthio)benzonitrile.
- 50 2-chloro-6-phenylsulphonylbenzonitrile.
- 2-chloro-6-phenylsulphonylbenzonitrile.
- 2-chloro-6-ethylsulphonylbenzonitrile.
- 2-chloro-6-chlorobenzylsulphonylbenzonitrile.
- 55 The benzonitrile derivatives obtainable by the process of the invention possess herbicidal activity, some being toxic to plant seeds and some to growing plants when applied as a

foliar spray or as a soil drench. The compounds were tested as herbicides in the following way:—

Aqueous compositions containing acetone (40v) water (60v), Triton X155 (0.5% w/v) and the benzonitrile derivative in logarithmically varying concentrations were used. The word "Triton" is a registered Trade Mark. In the soil spray and soil drench tests, imbibed seeds of oats and mustard and seedling plants of oats mustard and linseed, respectively, in sterile No. 1 John Innes compost, were sprayed at the rate of 50 gallons per acre or drenched at the rate of 1000 gallons per acre. In the foliage test, similar plants of oats, mustard and linseed were sprayed with a volume equivalent to 50 gallons per acre. Control tests in which seeds or plants were sprayed or drenched with the aqueous acetone—Triton X155 solution alone were also carried out. The phytotoxic effect of the benzonitrile derivative was assessed by determining the reduction from the control in fresh weight of stems and leaves of the test plants. The dosage required for 50% inhibition of shoot growth (GID 50) was obtained from a regression line relating percentage growth inhibition and dosage.

In the soil spray test, high selective toxicity was shown by 2-chloro-6-allyloxybenzonitrile and 2-chloro-6-(2-methoxyethoxy)benzonitrile whose GID 50 values against mustard were 6.7 and 9.8 pounds per acre respectively, compared with more than 10 pounds per acre against oats. 2-Chloro-6-(3-tolyloxy)benzonitrile, however, was more toxic to oats than to mustard, the respective GID 50 values being 3.6 and 8.0 pounds per acre.

In the foliar spray test, 2-chloro-6-isobutoxybenzonitrile had a GID 50 against linseed of 10 pounds per acre but more than 10 pounds per acre against mustard and oats. 2-Chloro-6-(2-methoxyethoxy)benzonitrile was selectively toxic to mustard, having a GID 50 of 2.4 pounds per acre compared with GID 50 of 9.2 and more than 10 pounds per acre against linseed and oats respectively. 2-Chloro-6-phenoxybenzonitrile was selectively toxic to oats, having a GID 50 of 3.0 pounds per acre, the GID 50 values against linseed and oats being more than 10 pounds per acre. 2-Chloro-6-(4-methoxyphenoxy)benzonitrile had GID 50 values against oats and mustard of 3.4 and 1.0 pounds per acre respectively compared with more than 10 pounds per acre against linseed. The treated plants showed epinasty. 2-Chloro-6-(3-trifluoromethylphenoxy)benzonitrile had GID 50 against mustard of 4.1 pounds per acre, compared with more than 10 pounds per acre against oats and linseed, and thus shows selective toxicity. The treated plants became bleached in appearance. High selective toxicity to mustard plants was also shown by 2-chloro-6-(3-methoxyphenoxy)benzonitrile,

2-chloro-6-(3-ethoxyphenoxy)benzonitrile and 2-chloro-6-(2-methoxyphenoxy)benzonitrile whose GID 50 values against mustard plants were respectively 2.8, 5.2 and 7.3 pounds per acre, the activity against the other test plants being negligible. 2-Chloro-6-(3-tolyloxy)benzonitrile also showed high selective toxicity to mustard plants, the GID 50 value being 2.1 pounds per acre, compared with more than 10 pounds per acre against oats and linseed.

In the soil drench test, 2-chloro-6-phenoxybenzonitrile was selectively toxic to linseed, the GID 50 value being 6.7 pounds per acre compared with over 10 pounds per acre for oats and mustard. 2-Chloro-6-(3-carboxyphenoxy)benzonitrile was selectively toxic to mustard, the GID 50 value being 7.5 pounds per acre compared with over 10 pounds per acre against oats and linseed. 2-Chloro-6-(3-tolyloxy)benzonitrile was selectively toxic to oats, the GID 50 value being 6.0 pounds per acre compared with more than 10 pounds per acre against mustard and linseed.

Some of the compounds prepared by the process of the invention also exhibit fungicidal activity.

Thus, in spore germination tests with spores of *Alternaria brassicicola* on wallflower leaves 95% inhibition of spore germination resulted when aqueous dispersions containing 0.005% Triton X100 as dispersion agent and 2000 parts per million (ppm) of 2-chloro-6-allylthiobenzonitrile, 2500 ppm of 2-chloro-6-(3-nitrophenoxy)benzonitrile or 1500 ppm of 2-chloro-6-(3-tolyloxy)benzonitrile were sprayed on the leaves prior to inoculation with the fungus spores and incubation.

Some compounds exhibit insecticidal activity. Thus, when an aqueous composition containing acetone (20% by volume), Triton X100 (0.05% by weight) and 2-chloro-6-(3-tolyloxy)benzonitrile (0.7% by weight) was sprayed on discs cut from the leaves of broad bean plants infested with the greenhouse red spider mite (*Tetranychus telarius*) at the rate of 38 gallons per acre, 100% kill of the mites was obtained. Some of the benzonitriles of the invention are also toxic to aquatic snails, particularly to *Australorbis glabratus*, *Planorbis corneus*, and *Bulinus truncatus* which are carriers of the parasite causing bilharziasis in man. Thus, 2-chloro-6-(2,4-dichlorophenoxy)benzonitrile and 2-chloro-6-(3-tolyloxy)benzonitrile each at a dosage of as little as 2 parts per million causes death to these snails in 24 hours. Accordingly, the invention further relates to a method of combatting aquatic snails which comprises treating said snails or their habitat with 2-chloro-6-(2,4-dichlorophenoxy)benzonitrile, or with 2-chloro-6-(3-tolyloxy)benzonitrile or a composition containing said compound.

The invention relates further to composi-

tions comprising a benzonitrile as hereinbefore specified and a carrier or a surface active agent, or carrier and a surface active agent.

The term "carrier" as used herein means a material, which may be inorganic or organic and synthetic or of natural origin, with which the active substance is mixed or formulated to facilitate its storage, transport and handling and its application to the plant, seed, soil or other object to be treated. The carrier is preferably biologically and chemically inert. It may be a solid or a fluid. Solid carriers are preferably particulate, granular or pelleted though other shapes and sizes are not thereby excluded. Solid carriers, generally obtainable in particulate, granular or pelleted form, may be naturally occurring minerals, though they may have been subjected to grinding, sieving, purification and other treatments, for example, gypsum, tripolite, diatomite, mineral silicates such as mica, vermiculite, talc and pyrophyllite and clays of the montmorillonite, kaolinite or attapulgite groups, calcium or magnesium limes or calcite and dolomite. Carriers produced synthetically, for example, synthetic hydrated silicon oxides and synthetic calcium silicates may also be used and many proprietary products of this type are available commercially. The carrier may also be an elemental substance such as sulphur or carbon, preferably an activated carbon. If the carrier possesses intrinsic catalytic activity such that it would decompose the toxicant it is advantageous to incorporate a stabilising agent.

For some purposes, a resinous or waxy carrier may be used, preferably one which is solvent soluble or thermoplastic, including fusible. Examples of such carriers are natural or synthetic resins such as a coumarone resin, rosin, copal, shellac, dammar, polyvinyl chloride, styrene polymers and copolymers, a solid grade of polychlorophenol such as is available under the Registered Trade Mark "Aroclor," a bitumen, an asphaltite, a wax, for example, beeswax or a mineral wax such as paraffin wax or Montan wax, or a chlorinated mineral wax. Compositions comprising such resinous or waxy carriers are preferably in granular or pelleted form.

Fluid carriers may be liquids, for example water, or an organic fluid including a liquefied normally vaporous or gaseous material, or a vaporous or gaseous material, and may be solvents or non-solvents for the active material. Horticultural petroleum spray oils boiling in the range of 275° to 575° F or boiling in the range 575° to 1000° F and having an unsulphonatable residue of at least 75% and preferably of at least 90%, or a mixture of these two types of oil are particularly suitable liquid carriers.

The carrier may also be a simple or compound fertiliser which may be a solid, pre-

ferably granular or pelleted, or a liquid, for example an aqueous solution.

The carrier may be mixed or formulated with the active material during its manufacture or at any stage subsequently. The carrier may be mixed or formulated with the active material in any proportion. One or more carriers may be used.

The compositions of the invention may be concentrates, suitable for storage or transport and containing, for example, from 10 to 95% by weight of the nitrile. These can be diluted with the same or a different carrier to a concentration suitable for application. The compositions of the invention may also be dilute compositions suitable for application. In general, concentrations of 0.01 to 0.5% by weight of active material based on the total weight of the composition are satisfactory, though lower and higher concentrations can be applied if necessary.

The compositions of the invention may be formulated as dusts. These comprise an intimate mixture of the nitrile and a finely powdered solid carrier such as is indicated above. These powder carriers may be oil-treated to improve adhesion to the surface to which they are applied. These dusts may be concentrates, in which case a highly sorptive carrier is preferably used. These required to be diluted with the same or a different finely powdered carrier, which may be of lower sorptive capacity, to a concentration suitable for application.

The compositions of the invention may be formulated as wettable powders comprising the nitrile mixed with a dispersing i.e., deflocculating or suspending, agent and, if desired, a finely divided solid carrier. The nitrile may be in particulate form or adsorbed on the carrier and preferably constitutes at least 10%, more preferably at least 50% by weight of the composition. The concentration of the dispersing agent should in general be between 0.1 and 10% by weight of the total composition though larger or smaller amounts may be used if desired.

The dispersing agent used in the composition of the invention may be any substance having definite dispersing, i.e., deflocculating or suspending, properties as distinct from wetting properties, although these substances may also possess wetting properties.

The dispersing agent used may be a protective colloid such as gelatin, glue, casein, gums or a synthetic polymeric material such as polyvinyl alcohol. Preferably, however, the dispersing agents used are sodium or calcium salts of high molecular weight sulphonc acids, e.g., the sodium or calcium salts of lignin sulphonc acids derived from sulphite cellulose waste liquors. The calcium or sodium salts of condensed aryl sulphonc acids, for

example the product known as "Tamol 731," are also suitable.

The dispersing agents used may be non-ionic emulsifiers, for example the condensation products of fatty acids containing at least 12, preferably 16 to 20, carbon atoms in the molecule, or of abietic acid or naphthenic acids obtained in the refining of petroleum lubricating oil fractions, with alkylene oxides such as ethylene oxide, or propylene oxide or with both ethylene oxide and propylene oxide as, for example, the condensation product of oleic acid and ethylene oxide containing 6 ethylene oxide units in the molecule. Partial esters of the above acids with polyhydric alcohols such as glycerol, polyglycerol, sorbitol or mannitol may also be used.

The dispersing agents referred to above may also possess wetting properties but in general it is preferably to incorporate two separate surface active agents, one having particularly good dispersing properties and the other having particularly good wetting properties. The actual amount of wetting agent incorporated can be varied considerably and in general is from 0 to 10% by weight based on the total composition.

Suitable wetting agents include the alkali metal salts, preferably sodium salts, of sulphuric acid esters or sulphonc acids containing at least 10 carbon atoms in the molecule, for example, the sodium secondary alkyl sulphates available under the Registered Trade Mark "Teepol," sodium salts of sulphonated castor oil, sodium dodecyl benzene sulphonate. Non-ionic wetting agents may also be employed for example, polyalkylene oxide polymers, e.g., the "Pluronic," and condensation products of polyalkylene oxides with aromatic nuclei (e.g., octyl cresol).

Granulated or pelleted compositions comprising a suitable carrier having a nitrile incorporated therewith are also included in the invention. These may be prepared by impregnating a granular carrier with a solution of the nitrile or by granulating a mixture of a finely divided solid carrier and the nitrile. The carrier used may consist of or contain a fertiliser or fertiliser mixture, for example superphosphate.

The composition of the invention may also be formulated as solutions of the nitrile (excluding 2-chloro-6-methoxybenzonitrile) in an organic solvent or mixture of solvents, for example alcohols, ketones, especially acetone, ethers, hydrocarbons. Petroleum hydrocarbon fractions used as solvents should preferably have a flash point about 73° F, for example, a refined aromatic extract of kerosine. For use in application of fungicidal compounds to foliage the solvent used should not be phytotoxic and for this purpose a petroleum spray oil boiling in the range 275° to 575° F or boiling in the range 575° to 1000° F

and having an unsulphonatable residue of at least 75% and preferably of at least 90%, or a mixture of these two types of oil, is preferably used. Auxiliary solvents such as alcohols, ketones and polyalkylene glycol ethers and esters may be used in conjunction with these petroleum solvents. Such oil solutions are particularly suitable for application by low volume spraying for example at the rate of 5 to 10 gallons per acre. They may also be diluted with a cheap solvent for high volume spraying.

Compositions of the present invention may also be formulated as emulsifiable concentrations which are concentrated solutions or dispersions of the nitrile in an organic liquid, preferably a water-insoluble organic liquid, containing an added emulsifying agent. These concentrates may also contain a proportion of water, for example up to 50% by volume, based on the total composition (i.e., a "mayonnaise" composition) to facilitate subsequent dilution with water. Suitable organic liquids are for example the above petroleum hydrocarbon fractions.

The emulsifying agent may be of the type producing water-in-oil type emulsions which are suitable for application by low volume spraying, or an emulsifier of the type producing oil-in-water emulsions may be used, producing concentrates which can be diluted with relatively large volumes of water for application by high volume spraying. In such emulsions the nitrile is preferably in the non-aqueous phase.

Suitable types of emulsifier for use in these emulsions or emulsifiable concentrates are the non-ionic and anionic dispersing and wetting agents described above, also suitable are long chain alkyl quaternary ammonium salts and alkyl sulpho-succinates.

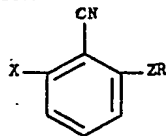
The concentration of emulsifier used will in general be within the limits 0.5% and 25.0% based on the final composition.

The compositions of the invention may contain other ingredients, for example, water conditioning agents for example, sodium polyphosphates or cellulose ethers, other herbicides, pesticides or stickers, for example a non-volatile oil.

Aqueous dispersions and emulsions, for example, compositions obtained by diluting the wettable powders or emulsifiable concentrates of the present invention with water also lie within the scope of the present invention.

WHAT WE CLAIM IS:—

1. A process for preparing a benzonitrile of the general formula



wherein X represents a chlorine or bromine atom, Z represents an oxygen or sulphur atom, or a sulphinyl SO or sulphonyl SO₂ group and R represents a hydrocarbon group which may be substituted by one or more of the following atoms or groups:— halogen, preferably chlorine, trifluoromethyl, nitro, amino, acylamino, hydroxy, hydrocarbyloxy, the group OCH₂CH₂OR¹ (wherein R¹ represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms), carboxyl or hydrocarbyloxycarbonyl, which comprises treating a 2-chloro-6-nitrobenzonitrile or 2-bromo-6-nitrobenzonitrile with a compound of formula MZ'R wherein M represents an alkali metal or ammonium, or with a mixture of a compound of formula HZ'R and an alkali metal hydroxide, an alkali metal hydride, ammonia or ammonium hydroxide, Z' representing an oxygen or sulphur atom and R having the aforesaid meaning, and thereafter, if the corresponding sulphinyl derivative is required oxidising the resulting thio derivative, or if the sulphonyl derivative is required, oxidising the resulting thio or sulphinyl derivative.

2. A process as claimed in claim 1 wherein R represents an aliphatic hydrocarbon group of 1 to 4 carbon atoms, or an aryl derivative thereof, which may be substituted as aforesaid.

3. A process as claimed in claim 2 wherein R is attached to Z by a primary or secondary carbon atom.

4. A process as claimed in claim 1 wherein R represents an aromatic hydrocarbon group which may be substituted as aforesaid.

5. A process as claimed in claim 4 wherein R represents a methoxyphenyl group.

6. A process as claimed in any one of the preceding claims wherein the hydrocarbyl radical of the hydrocarbyloxy or hydrocarbyloxycarbonyl group is an aliphatic hydrocarbon radical of 1 to 4 carbon atoms, or an aromatic hydrocarbon radical.

7. A process as claimed in any one of the preceding claims wherein a mixture of the 2-halo-6-nitrobenzonitrile and the compound MZR or the compound HZR and an alkali metal hydroxide is heated at a temperature in the range 120° to 250° C. in the absence of a solvent.

8. A process as claimed in any one of claims 1 to 6 wherein an inert liquid reaction medium is used.

9. A process as claimed in any one of the preceding claims wherein the oxidising agent used in the preparation of the sulphinyl or sulphonyl derivative is a percarboxylic acid or hydrogen peroxide or a mixture of hydrogen peroxide and a carboxylic acid.

10. A process as claimed in claim 9 wherein the oxidising agent is a mixture of acetic acid and hydrogen peroxide or peracetic acid.

11. A process for preparing benzonitriles

- substantially as hereinbefore described with reference to the Examples.
12. Benzonitriles whenever prepared by the process claimed in any one of the preceding claims.
13. Benzonitriles having the general formula claimed in any one of claims 1 to 6, excluding 2-chloro-6-methoxybenzonitrile.
14. 2-Chloro-6-allyloxybenzonitrile.
15. 2-Chloro-6-isopropoxybenzonitrile.
16. 2-Chloro-6-isobutoxybenzonitrile.
17. 2-Chloro-6-benzyloxybenzonitrile.
18. 2 - Chloro - 6 - (2 - methoxyethoxy)-benzonitrile.
19. 2 - -Chloro - 6 - (2 - hydroxyethoxy)-benzonitrile.
20. 2-Chloro-6-phenoxybenzonitrile.
21. 2 - Chloro - 6 - (2,4 - dichlorophenoxy)benzonitrile.
22. 2 - Chloro - 6 - (3 - nitrophenoxy)-benzonitrile.
23. 2 - Chloro - 6 - (4 - methoxyphenoxy)-benzonitrile.
24. 2 - Chloro - 6 - (3 - trifluoromethylphenoxy)benzonitrile.
25. 2 - Chloro - 6 - (3 - methoxycarbonylphenoxy)-benzonitrile.
26. 2 - Chloro - 6 - (3 - carboxyphenoxy)-benzonitrile.
27. 2 - Chloro - 6 - (4 - aminophenoxy)-benzonitrile.
28. 2 - Chloro - 6 - (4 - acetylaminophenoxy)benzonitrile.
29. 2 - Chloro - 6 - (4 - chlorophenoxy)-benzonitrile.
30. 2 - Chloro - 6 - (2 - chlorophenoxy)-benzonitrile.
31. 2-Chloro-6-(4-tolyloxy)benzonitrile.
32. 2 - Chloro - 6 - (1 - naphthyloxy)-benzonitrile.
33. 2 - Chloro - 6 - (2 - naphthyloxy)-benzonitrile.
34. 2-Chloro-6-phenylthiobenzonitrile.
35. 2-Chloro-6-(4-tolylthio)benzonitrile.
36. 2 - Chloro - 6 - (4 - chlorophenylthio)-benzonitrile.
37. 2-Chloro-6-benzylthiobenzonitrile.
38. 2-Chloro-6-allylthiobenzonitrile.
39. 2 - Chloro - 6 - (ethoxycarbonylmethylthio)benzonitrile.
40. 2 - Chloro - 6 - (4 - chlorobenzylthio)benzonitrile.
41. 2 - Chloro - 6 - phenylsulphonylbenzonitrile.
42. 2 - Chloro - 6 - phenylsulphonylbenzonitrile.
43. 2 - Chloro - 6 - ethylsulphonylbenzonitrile.
44. 2 - Chloro - 6 - (4 - chlorobenzylsulphonyl)benzonitrile.
45. A composition comprising benzonitrile claimed in any one of claims 13 to 44 and a carrier as hereinbefore defined or a surface active agent.
46. A composition as claimed in claim 45 comprising a carrier as hereinbefore defined and a surface active agent.
47. A composition as claimed in claim 45 formulated as a dust and comprising an intimate mixture of the benzonitrile and a finely powdered carrier.
48. A composition as claimed in claim 46 formulated as a wettable powder comprising said benzonitrile, a dispersing agent and, if desired, a finely divided solid carrier.
49. A composition as claimed in claim 45 comprising said benzonitrile and an inorganic, resinous or waxy carrier in the form of granules or pellets.
50. A composition as claimed in claim 45 which is a solution of said benzonitrile, excluding 2-chloro-6-methoxybenzonitrile, in a solvent or solvent mixture.
51. A composition as claimed in claim 46 which is an emulsifiable concentrate comprising said benzonitrile, a solvent therefore and an emulsifier.
52. A composition as claimed in claim 45 or 46 which is an aqueous dispersion or emulsion of said benzonitrile.
53. Aqueous compositions obtained by diluting the wettable powders or emulsifiable concentrates of claims 48 or 51 with water.
54. Compositions as claimed in claim 45 or 46 substantially as hereinbefore described with reference to the tests.
55. A method of eradicating undesirable fungi from plants which comprises treating said fungi and/or plants with 2-chloro-6-allylthiobenzonitrile, 2-chloro-6-(3-nitrophenoxy)benzonitrile or 2-chloro-6-(3-tolyloxy)benzonitrile either *per se* or as a composition claimed in any one of claims 45 to 54.
56. A method of eradicating undesirable insects from plants which comprises treating said insects and/or plants with 2-chloro-6-(3-tolyloxy)benzonitrile either *per se* or as a composition claimed in any one of claims 45 to 54.
57. A method of combatting aquatic snails which comprises treating the snails and/or their habitat with 2-chloro-6-(2,4-dichlorophenoxy) benzonitrile or 2-chloro-6-(3-tolyloxy)benzonitrile either *per se* or as a composition claimed in any one of claims 45 to 54.

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